Electrochimica Acta 187 (2016) 422–432

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Comparative study on experiments and simulation of blended cathode active materials for lithium ion batteries

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ARTICLE INFO

Article history:
Received 13 October 2015
Received in revised form 5 November 2015
Accepted 6 November 2015
Available online 15 November 2015

Keywords:
Simulation
blended cathode active materials
experiment
lithium ion battery

ABSTRACT

We simulate the electrochemical properties of Li-ion cells consisting of a blended cathode composed of $LiMn_2O_4$ and $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ and an artificial graphite anode using the Li-ion battery model available in COMSOL MULTIPHYSICS 4.4 along with a capacity fade model. The discharge profiles of the pure and blended cathodes at various current rates obtained through simulations and experimental results are well matched. By combining two capacity fade models available in literature, namely the solid electrolyte interphase (SEI) growth model and the Mn^{2+} dissolution model, the cycling performance of the pure $LiMn_2O_4$ cells at 25 °C are successfully simulated and found to be in a good agreement with the experimental results. The blended cathode exhibits better capacity retention than the pure $LiMn_2O_4$ during cycling. We also observed that at high powers, the gravimetric energy density of the $LiMn_2O_4$ cathode exceeds that of the $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathode; the reverse effect is seen at low powers. Further, we were able to easily modulate the energy and power densities of the blended cathode system by changing the blend ratio in our simulation model.

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1. Introduction

Li-ion batteries (LIBs) have been adopted in various types of electric vehicles (xEVs) such as hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), and electric vehicles (EVs) as a substitute for Ni-metal hydride batteries (Ni-MHs), owing to their higher energy density than Ni-MHs as well as a comparable calendar and cycle life [1]. However, regardless of the issues related to cost and safety, the energy densities of LIBs need to be improved continuously in order to meet the mileage requirements as far as conventional vehicles having internal combustion engines are concerned. This problem can be easily addressed if novel electrode active materials with high energy densities are developed. However, there are only a few commercially available cathode active materials for this purpose, such as $LiCoO_2$, $LiNi_xCo_yMn_zO_2$, $LiMn_2O_4$, and $LiFePO_4$ and anode active materials such as graphite, amorphous carbons, and $Li_4Ti_5O_{12}$. Therefore, in order to fulfill the challenging requirements of large-format LIBs for xEVs, blended electrode active materials have been developed.

Among the blended electrode active materials, systems composed of $LiMn_2O_4$ and $LiNi_xCo_yMn_zO_2$ have been extensively investigated owing to their synergetic performance from the point of view of power and energy densities. While $LiMn_2O_4$ shows the best rate performance at a low cost, it also has a low discharge specific capacity and a poor high temperature performance [2–6]. Therefore, in a blended electrode system, the low energy density and poor reliability of $LiMn_2O_4$ should be compensated by another cathode active material that has a high energy density such as $LiNi_xCo_yMn_zO_2$. For instance, in order to fulfill high energy density requirements for a 40 mile drive, LG Chem has already developed $LiMn_2O_4$/$LiNi_xCo_yMn_zO_2$-based LIBs for GM Chevy Volt, which was the first PHEV released in the market in 2010/2011.

There are many previous works investigating the reasons behind the good electrochemical performances of blended systems. H. Y. Trans investigated the blended system composed of $LiMn_2O_4$ and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, where the two materials were selected to compensate for the demerits of each other. $LiMn_2O_4$ has a low discharge capacity and a poor cycle life at high temperatures, whereas $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ has a poor rate capability and thermal stability [7]. In particular, it is very impressive that $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ is able to suppress the Mn^{2+} dissolution efficiently, which results in good cycle life at high temperatures. This phenomenon has already been discovered and discussed by T. Numata [9]. In their study, Mn^{2+} dissolution from a blend of

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http://dx.doi.org/10.1016/j.electacta.2015.11.029
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Nomenclature

a	specific surface area, $\mathrm{m^{-1}}$
D	diffusion coefficient, $\mathrm{m^2\,s^{-1}}$
I_{app}	applied current density, $\mathrm{A\,m^{-2}}$
i_{os}	exchange current density for side reaction, $\mathrm{A\,m^{-2}}$
j	pore wall flux of lithium ions, $\mathrm{mol\,m^{-2}\,s^{-1}}$
j_s	local volumetric current density for side reaction, $\mathrm{A\,m^{-2}}$
k	electrochemical reaction rate constant, $\mathrm{m^{2.5}\,mol^{-0.5}\,s^{-1}}$
k_0	frequency factor, $\mathrm{s^{-1}}$
L	thickness of battery component, m
R_{film}	film resistance at the electrode/electrolyte interface, $\Omega\,\mathrm{m^2}$
R_P	resistance of the film products, $\Omega\,\mathrm{m^2}$
t_+	cation transference number
x	main dimension across the cell sandwich
ε	volume fraction
η	local over potential, V
κ	electrolyte conductivity, $\mathrm{S\,m^{-1}}$
σ	electrode conductivity, $\mathrm{S\,m^{-1}}$
δ_{film}	film thickness, m
φ	electric potential, V

Subscript

1	solid phase
2	solution phase
e	electrolyte
n	negative electrode
p	positive electrode
P	Side reaction product
–	to the left of an interface
+	to the right of an interface
s	side reaction

$Li_yMn_2O_4$ and 10 wt% $Li_yNi_{0.80}Co_{0.2}O_2$ was significantly reduced compared to the dissolution from pure $Li_yMn_2O_4$. H. Kim [8] also blended $Li_{1.1}Mn_{1.9}O_4$ and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ in a 1:1 weight ratio, and found that the blend exhibited good capacity retention values compared to pure $Li_{1.1}Mn_{1.9}O_4$. They concluded that the addition of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ enhanced the capacity retention of $Li_{1.1}Mn_{1.9}O_4$. Besides the studies cited above, many other studies have been published on blended cathode systems consisting of cathode active materials in order to achieve balanced or synergetic properties in LIBs [8–14].

However, it is time-consuming and expensive to find optimum blend chemistry and blend ratio solely through experimentation. In this context, simulation tools would provide an efficient method to predict the electrochemical behavior of various blends. P. Albertus [15] compared the simulated and experimental galvanostatic discharge performances of coin cells containing $Li_yMn_2O_4$ and $Li_yNi_{0.8}Co_{0.15}Al_{0.05}O_2$ blended cathodes with different blend ratios over a wide range of discharge rates. They also compared the experimental and theoretical impedance spectra by adopting a modified dual foil model to handle particles made of different active materials, radii, film resistances, and particle conductive matrix contact resistances. They assumed equal thicknesses of the two active systems and their blends as well as equal electrolyte volume fractions. However, they also used half-cells with Li metal as the anode. Hence, they were unable to complete life studies on the cells.

P. Ramadas [16] developed a capacity fade model by incorporating side reactions with the existing Li-ion intercalation model and used it to simulate the cycle performance of $LiCoO_2$. However, they did not validate their calculated results with experimental values. J. Park [17] also derived models for predicting the volume fraction changes in electrodes due to Mn dissolution and extended the porous electrode theory to correlate the Mn^{2+} dissolution with the capacity fade in LIBs. They used the model to simulate the cycle performance of $LiMn_2O_4$ and mapped the effects of Mn^{2+} dissolution on the capacity fading during cycling under different temperature and cell potential range conditions.

To the best of our knowledge, blended cathode systems consisting of $LiMn_2O_4$ and $Li(Ni_{0.6}Co_{0.2}Mn_{0.2})O_2$ (NCM622) have not been studied. In particular, NCM622 has been extensively explored as a promising layered oxide, since it delivers the highest discharge capacity among the commercial layered oxides, although it has poor thermal stability. However, the capacity fading behavior, which is the most challenging parameter to predict, has not been investigated extensively for the NCM622 cathode systems as well as the synergetic effects of the two pure cathode materials on each other. In this work, we simulate the electrochemical properties of pure and blended cathodes composed of $LiMn_2O_4$ and NCM622 by adopting the LIB model available in COMSOL MULTIPHYSICS 4.4, along with the previously developed capacity fade models by P. Ramadas and J. Park [16,17]. The results from the simulations are also compared with experimental data, which were obtained using coin-type full cells at 25 °C. In particular, the cycle life of pure and blended cathodes is discussed by considering both SEI growth and Mn^{2+} dissolution behavior.

2. Experimental

The two cathode active materials used in this study are $LiMn_2O_4$ obtained from Iljin materials, Korea and $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ obtained from L & F, Korea. In order to examine electrochemical properties in experiments, we manufactured 2032 coin-type full cells with cathodes of three different blend ratios of $LiMn_2O_4$ and $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ and artificial graphite (Showa Denko, Japan) as the anode. The composition of the cathodes were 90 wt% blended active materials, 5 wt% electric conductor (Super-P, Timcal, Switzerland) and 5 wt% poly(vinylidene fluoride) (PVdF, Kureha, Japan) as a binder. *N*-methyl pyrrolidone (NMP, Sigma Aldrich, USA) was used as the solvent for electrode slurry. The cathode slurry was cast onto an aluminum foil (15 μm thickness, Sam A Aluminum, Korea) using the doctor blade technique and then dried at 120 °C for 1 h to evaporate the solvent. Furthermore, the punched electrodes were additionally dried at 60 °C under vacuum to remove all the NMP and water residues in the electrode. Scanning electron microscopy (SEM, S4800, Jeol, Japan) was used to investigate the surface morphology of the electrodes. Three different blended cathodes with approximately equal loading density were prepared as shown in Table 1. To ensure similar liquid-phase effects in the cell, the electrode thickness as well as the electrode porosity was controlled to be equal. Five cells of each cathode composition were built, and their relative standard deviations were around 0.5 %.

When assembling the coin-type full cells, we used PE separators (ND420, Asahi Kasei E-Materials, Japan) and liquid electrolytes consisting of 1.15 M $LiPF_6$ in an ethylene carbonate and ethylmethyl carbonate mixture (3/7 by volume, PANAX ETEC, Korea). The assembled cells were aged for 12 h and then cycled at a constant current (CC) of C/10 rate in both charging and discharging processes as a formation step using a charge/discharge cycler (PNE Solutions, Korea) at 25 °C. The formation step was followed by a stabilization step at a C/5 rate for 3 cycles. Rate capability test was conducted on three cells of each cathode composition at C/5, C/2, 1C, 3C, 5C, 7C, 10C and 12C constant current mode for three cycles each. The various discharge processes at different C-rates were

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